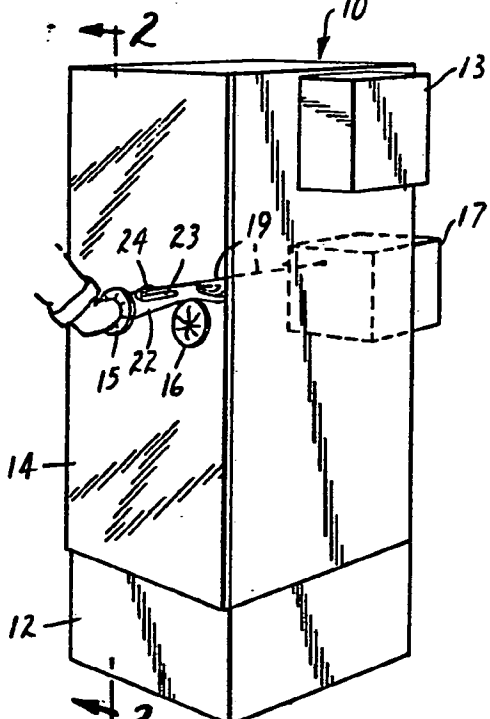
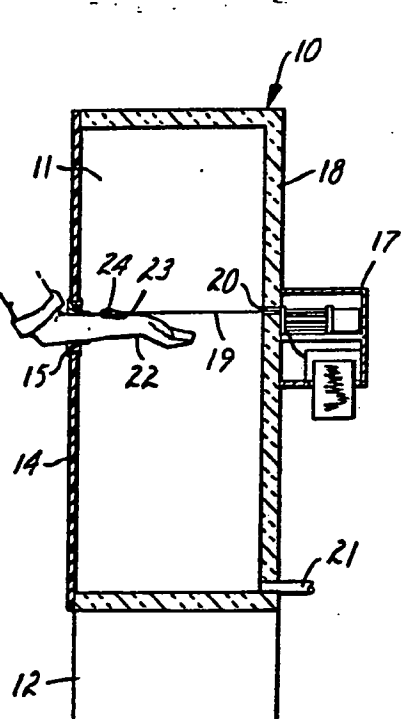




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| (54) Title: ADHESIVE AND ADHESIVE-COATED SHEET MATERIAL FOR MOIST SKIN | | |
| <div style="display: flex; justify-content: space-around; align-items: flex-start;">   </div> | | |
| <p>(57) Abstract</p> <p>A pressure-sensitive adhesive and a pressure-sensitive adhesive-coated sheet material exhibiting an initial dry skin adhesion value of at least about 0.75 Newton per 100 millimeters of width, a dry skin adhesion value after 48 hours of not more than about 12 Newtons per 100 millimeters of width, and a moist skin adhesion value of at least about 2.2 Newtons per 100 millimeters of width.</p> | | |

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ADHESIVE AND ADHESIVE-COATED SHEET
MATERIAL FOR MOIST SKIN

Technical Field

5 The present invention relates to normally tacky pressure-sensitive adhesive compositions and sheet materials coated therewith.

Background of the Invention

10 The critical requirements of adhesion to dry skin place many constraints on the bond-making and bond-breaking capabilities of the adhesive being employed. Not only must initial adhesion to skin be satisfactory, but adherence over an extended period of time is necessary, and this requires relatively high shear adhesion in order that
15 movement of the underlying skin may be withstood. The problem of providing suitable adhesion to skin is further complicated by the requirement that the adhesive should release without injury to or irritation of skin, and should not leave a residue on skin when the adhesive bandage or
20 the like is removed therefrom. Pressure-sensitive adhesives which meet all of the requirements of industrial and domestic applications generally fall short of the requirements of an adhesive which is to be employed in a medical or surgical use involving adhesion to skin, and
25 only a select few of the commercially available pressure-sensitive adhesives are actually completely acceptable for such use.

 An adhesive which is to be employed on skin may be expected to experience moisture found on the skin.
30 Moisture may be experienced as the result of physiological changes involving skin or underlying tissue. For example, the adhesive may experience perspiration or tissue or wound exudate which is found on skin prior to application of the adhesive bandage or the like thereto or which appears
35 subsequently to such application. Moisture may also be experienced by an adhesive as the result of cleansing of



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skin which may precede application of an adhesive bandage or surgical incise drape thereto, and current practice generally requires that the skin be allowed to dry thoroughly prior to such an application. Moisture may further be experienced during routine cleansing of skin adjacent to the site of an adhesive bandage or the like. Finally, an adhesive may experience moisture as the result of environmental changes involving, for example, condensation of air-borne moisture on skin.

When the bond-making and bond-breaking requirements of an adhesive which is intended for employment on dry skin are compounded by adding the requirement that the adhesive adhere suitably to moist skin, the balancing of the physical properties of the adhesive becomes much more critical. The adhesive, while retaining the properties of suitable shear adhesion and ease of removal, must exhibit the wholly different property of suitable adhesion to moist skin. Further, in order to be useful in a variety of applications, that adhesive should retain the property of suitable adhesion to dry skin. Such versatility requires that the adhesive exhibit a proper balance of hydrophobic and hydrophilic properties.

Acrylic pressure-sensitive adhesives have been known for years and have found applications in many fields including medical or surgical uses. Notable among such adhesives are certain of the generally hydrophobic acrylic copolymers of U.S. Patent No. 2,884,126/RE 24,906 (Ulrich) which have been employed in surgical tapes such as the breathable surgical adhesive tapes of U.S. Patent No. 3,121,021 (Copeland). While these adhesives and tapes exhibit the many desirable attributes which permit their successful employment in many medical and surgical uses, their adhesion to moist skin could be improved upon.

Thus, there is a need for a pressure-sensitive adhesive (and a pressure-sensitive adhesive-coated sheet material) which exhibits improved adhesion to moist skin, while at the same time retaining properties of suitable



adhesion to dry skin, suitable shear strength, ease of removal from skin without adhesive splitting, and dermatological acceptability.

Brief Summary of the Invention

5 The present invention provides a novel adhesive-coated sheet material having a backing member and a coating covering at least a portion of one major surface thereof of a pressure-sensitive adhesive composition comprising a copolymer consisting essentially of copolymerized A, B and
10 C monomers as follows:

A is a hydrophobic monomeric acrylic acid ester of a non-tertiary alcohol, said alcohol having from 4 to about 14 carbon atoms;

15 B is a hydrophilic monomer which has a vinyl group copolymerizable with the A monomer and is other than acrylic acid, methacrylic acid, itaconic acid, acrylamide, methacrylamide, lower alkyl-substituted acrylamide, and N-vinyl-2-pyrrolidone, the amount by weight of
20 B monomer being about 5 to 30% of the total weight of all monomers in the copolymer; and

C is at least one polar monomer copolymerizable with the A and B monomers, selected from the group consisting of acrylic acid, methacrylic
25 acid, itaconic acid, acrylamide, methacrylamide, lower alkyl-substituted acrylamide, and N-vinyl-2-pyrrolidone, the amount by weight of C monomer being about 0.5 to 30% of the total weight of all monomers in the copolymer;

30 wherein the A, B and C monomers are copolymerized to form a polymeric backbone and the combination of A, B and C monomers being such as to provide the sheet material with an initial dry skin adhesion value of at least about 0.75
35 Newton per 100 millimeters of width, a dry skin adhesion value after 48 hours of not more than about 12 Newtons per 100 millimeters of width, and a moist skin adhesion value



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of at least about 2.2 Newtons per 100 millimeters of width.

The present invention also provides a novel adhesive copolymer consisting essentially of copolymerized A, B and C monomers as follows:

- 5 A is a hydrophobic monomeric acrylic acid ester of a non-tertiary alcohol, said alcohol having from 4 to about 14 carbon atoms;
- 10 B is a hydrophilic monomer which has a vinyl group copolymerizable with the A monomer and is other than acrylic acid, methacrylic acid, itaconic acid, acrylamide, methacrylamide, lower alkyl-substituted acrylamide, and N-vinyl-2-pyrrolidone, the amount by weight of B monomer being about 5 to 30% of the total weight of all monomers in the copolymer; and
- 15 C is at least one polar monomer copolymerizable with the A and B monomers, selected from the group consisting of acrylic acid, methacrylic acid, itaconic acid, acrylamide, methacrylamide, lower alkyl-substituted acrylamide, and N-vinyl-2-pyrrolidone, the amount by weight of C monomer being about 0.5 to 30% of the total weight of all monomers in the copolymer;
- 20 wherein the A, B and C monomers are copolymerized to form a polymeric backbone and the combination of A, B and C monomers being such as to be able to provide an adhesive-coated sheet material which has an initial dry skin adhesion value of at least about 0.75 Newton per 100 millimeters of width, a dry skin adhesion value after
- 25 48 hours of not more than about 12 Newtons per 100 millimeters of width, and a moist skin adhesion value of at least about 2.2 Newtons per 100 millimeters of width.
- 30 The preferred B monomer is a hydrophilic macromolecular monomer, and the preferred hydrophilic macromolecular monomer has the general formula X-Y-Z, wherein

35 The preferred B monomer is a hydrophilic macromolecular monomer, and the preferred hydrophilic macromolecular monomer has the general formula X-Y-Z, wherein



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X is a vinyl group copolymerizable with the A monomer;

Y is a divalent linking group; and

Z is a monovalent polymeric moiety comprising a polyether essentially unreactive under copolymerizing conditions.

5 The pressure-sensitive adhesives and pressure-sensitive adhesive-coated sheet materials of the invention exhibit a balance of properties which render them particularly useful in medical and surgical applications involving adhesion to skin. These adhesives and adhesive-coated sheet materials adhere suitably to moist skin. These adhesives and adhesive-coated sheet materials further possess all of the other attributes required of a suitable adhesive or adhesive-coated sheet material for use in applications involving adhesion to skin. Specifically, these adhesives and adhesive-coated sheet materials exhibit suitable initial adhesion to dry skin and may be removed from skin without injury thereto or undesirable irritation thereof.

20 Preferred adhesives and adhesive-coated sheet materials of the invention further exhibit a moist-skin adhesion value of at least about 3 Newtons per 100 millimeters of width. Most preferred adhesives and adhesive-coated sheet materials exhibit a moist-skin adhesion value of at least about 4 Newtons per 100 millimeters, thereby rendering them useful in what have heretofore been particularly troublesome applications. Certain of these adhesives and adhesive-coated sheet materials also exhibit an initial dry skin adhesion value of at least about 2 Newtons per 100 millimeters of width and/or an initial dry skin adhesion value after 48 hours of not more than about 8 Newtons per 100 millimeters of width.

30 The desirable balance of properties exhibited by the adhesives and adhesive-coated sheet materials of the invention results from the selection of certain types of monomers and employment of particular amounts thereof in



preparing the pressure-sensitive adhesive copolymer. As noted above, the adhesive copolymer comprises a hydrophobic monomer A, a hydrophilic monomer B and a polar monomer C. The A monomer is believed to contribute hydrophobicity to the copolymer, and in combination with the C monomer, provides a versatile pressure-sensitive adhesive which exhibits suitable adhesion performance on dry skin. The B monomer is believed to contribute hydrophilicity to the copolymer and to plasticize the adhesive copolymer. It is the inclusion of the B monomer which results in an adhesive exhibiting suitable adhesion to moist skin. Finally, the C monomer is believed to reinforce the copolymer, thereby providing suitable internal (cohesive) strength, and to also contribute to the hydrophilicity of the copolymer. It is only through proper selection of monomers and amounts thereof that an adhesive copolymer results which exhibits suitable initial adhesion to dry skin, suitable ease of removal, and suitable adhesion to moist skin.

The desirable balance of properties exhibited by the adhesive and adhesive-coated sheet material of the present invention is achieved using a single pressure-sensitive adhesive copolymer. No additives are required which could migrate and thereby irritate underlying skin or impair adhesive performance, or which could cause formulation problems due to their incompatibility with other components.

The adhesives of the invention may be desirably incorporated into and the adhesive-coated sheet materials of the invention embodied desirably as, for example, an adhesive tape, adhesive strip, wound dressing, monitoring or neuro-stimulating electrode, or surgical drape which are intended for attachment to skin. Such tape, strip, dressing, electrode and drape devices would be versatile since they could be used both on dry skin or skin which is (or expected to become) moist.



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Brief Description of the Drawings

Figure 1 illustrates a perspective view of a constant temperature/humidity chamber useful for determining moist skin adhesive performance; and

5 Figure 2 is a cross-sectional view taken substantially along line 2-2 of Fig. 1 with some parts shown in full.

Detailed Description of the Invention

10 The phrase "lower alkyl" as used throughout the instant specification and claims designates straight or branched-chain alkyl groups containing 1 to about 6 carbon atoms. The preferred "lower alkyl" groups contain 1 to about 4 carbon atoms.

15 As indicated above, the A monomer of the pressure-sensitive adhesive copolymer is a hydrophobic acrylic acid ester of a non-tertiary alcohol, which alcohol contains 4 to about 14 carbon atoms and preferably about 6 to 12 carbon atoms. It is preferred that the non-tertiary alcohol be an alkyl alcohol. By the use of the term
20 "hydrophobic" in connection with the A monomer is meant that the A monomer lacks substantial affinity for water.

Examples of suitable monomers for use as the A monomer include the esters of acrylic acid or methacrylic acid with non-tertiary alcohols such as 1-butanol,
25 2-butanol, 1-pentanol, 2-pentanol, 3-pentanol, 2-methyl-1-butanol, 1-hexanol, 2-hexanol, 2-methyl-1-pentanol, 3-methyl-1-pentanol, 2-ethyl-1-butanol, 3,5,5-trimethyl-1-hexanol, 3-heptanol, 1-octanol, 2-octanol, isooctyl alcohol, 2-ethyl-1-hexanol, 1-decanol, 1-dodecanol,
30 1-tridecanol, 1-tetradecanol and the like. The preferred A monomer is the ester of acrylic acid with isooctyl alcohol.

It is to be understood that the pressure-sensitive adhesive copolymer may comprise a single type of A monomer or may comprise two or more different A monomers.

35 Monomer B of the pressure-sensitive adhesive is a hydrophilic monomer which has a vinyl group copolymerizable



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with the A and C monomers and is other than acrylic acid, methacrylic acid, itaconic acid, acrylamide, methacrylamide, lower alkyl-substituted acrylamide and N-vinyl-2-pyrrolidone. By the use of the term "hydrophilic" in connection with the B monomer is meant that the B monomer has substantial affinity for water. It is preferred that the B monomer contain one and only one vinyl group copolymerizable with the A and C monomers.

As indicated above, monomer B is preferably a hydrophilic macromolecular monomer containing a plurality of hydrophilic sites which impart the required hydrophilicity to the monomer.

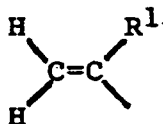
As also indicated above, monomer B of the pressure-sensitive adhesive copolymer is most preferably a hydrophilic macromolecular monomer of the general Formula I



I

wherein X is a vinyl group copolymerizable with the A and C monomers, Y is a divalent linking group, and Z is a monovalent polymeric moiety comprising a polyether essentially unreactive under the free-radical-initiated, copolymerizing conditions employed to form the pressure-sensitive adhesive copolymer.

The preferred X group of the B monomer of Formula I above is of the general formula II



II

wherein R^1 is a hydrogen atom or a methyl group.

The preferred Y group of the B monomer of Formula

I above is a $\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}- \end{array}$ group (i.e., a divalent carbonyl group).

The preferred Z moiety of the B monomer of Formula I above is a monovalent polyether of the general formula III



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-W-OR²

III

5 wherein R² is hydrogen, lower alkyl, phenyl, or substituted phenyl; and W is a divalent poly(lower alkylene oxide) group containing 2 to about 250 repeating alkoxy units and selected from the group consisting of a poly(ethylene oxide) radical, a poly(propylene oxide) radical, a radical of a copolymer of ethylene oxide and propylene oxide, and a polytetrahydrofuran radical. In a most preferred B monomer of Formula I, a monovalent polyether of Formula III is
10 bonded covalently to the carbonyl group (i.e., where Y is divalent carbonyl) through a terminal oxygen atom contained in the W moiety.

15 Preferably, the W moiety of Formula III contains about 5 to 250 repeating alkoxy units. More preferably, the W moiety contains about 5 to 125 repeating alkoxy units. Most preferably, the W moiety contains about 5 to 25 repeating alkoxy units.

20 The most preferred W moiety of Formula III is a poly(ethylene oxide) radical, a poly(propylene oxide) radical, or a radical of a copolymer of ethylene oxide and propylene oxide.

25 A variety of B monomers are available commercially. For example, commercially available B monomers which have been found to be suitable are the 2-(2-ethoxyethoxy)ethyl acrylate which is available under the trade designation "SR-256" from Sartomer Company, West Chester, PA; the methoxy poly(ethylene oxide)₁₀ acrylate which is available under the trade designation "No. 8816" from Monomer-Polymer & Dajac Laboratories, Inc., Trevose, PA; the methoxy poly(ethylene oxide) methacrylates of 200 Daltons, 400 Daltons, and 1000 Daltons which are available under the trade designations "No. 16664", "No. 16665" and "No. 16666", respectively, from Polysciences, Inc., Warrington, PA; the hydroxy poly(ethylene oxide)₅
30 methacrylate which is available under the trade designation "No. 16712" from Polysciences, Inc., Warrington, PA.
35



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Other preferred B monomers may be prepared using commercially available starting materials and conventional methods. For example, the preferred B monomers wherein R² of Formula III is lower alkyl may be prepared by reacting an α,β -unsaturated carboxylic acid such as acrylic acid or methacrylic acid with an equimolar amount of mono-alcohol of a poly(lower alkylene oxide). The esterification reaction is generally conducted under anhydrous conditions in an organic solvent which preferably will form an azeotropic mixture with the water which is generated as the esterification reaction proceeds. A suitable solvent is toluene. Typically, the alcohol is combined with the organic solvent and the unsaturated carboxylic acid is then added thereto. In the event that the alcohol is a solid at room temperature, it is first melted by heating prior to addition of the unsaturated carboxylic acid. The reaction is conducted in the presence of an acid catalyst such as para-toluenesulfonic acid and a free-radical inhibitor such as copper powder. The reaction mixture is refluxed for generally 16 to 18 hours under nitrogen, and the water generated is removed using, for example, a Dean Stark trap.

Examples of suitable mono-hydroxyl-terminated poly(lower alkylene oxides) which may be used to prepare the preferred B monomers using the above-described procedure include Carbowax[®] 350, Carbowax[®] 550, Carbowax[®] 750, Carbowax[®] 2000 and Carbowax[®] 5000 (i.e., the methoxy-poly(ethylene oxide) ethanols of about 350 MW, 550 MW, 750 MW, 2000 MW and 5000 MW, respectively, commercially available from Union Carbide Corp); a monoalcohol of a polytetrahydrofuran of about 16,000 MW prepared as described in connection with the preparation of Monomer "B-9" in the Examples below; UCON[®] LB-285 (an n-butoxy poly(propylene oxide) propanol having about a 1000 MW, commercially available from Union Carbide Corp.); UCON[®] 50-HB260 (an n-butoxy poly(ethylene oxide/propylene oxide) [50:50 by weight] alcohol having about a 1000 MW, available from Union Carbide Corp.); and Pycal[®] 94 (a phenoxy



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poly(ethylene oxide)₄ ethanol, available from Atlas Chemical Industries.).

5 B monomers wherein R² is hydrogen may be prepared by reacting an α,β -unsaturated carboxylic acid or hydroxyalkyl ester with an anhydride selected from monoepoxides, lactones or mixtures thereof as taught in U.S. Patent No. 4,126,527, incorporated herein by reference.

10 The preferred B monomer for employment in preparing the pressure-sensitive adhesive copolymer is the acrylate ester of above-described Carbowax® 750.

It is to be understood that the pressure-sensitive adhesive copolymer may comprise a single type of B monomer or may comprise two or more different B monomers.

15 The C monomer is a polar monomer which is copolymerizable with the A and B monomers. The C monomer is selected from the group consisting of acrylic acid, methacrylic acid, itaconic acid, acrylamide, methacrylamide, lower alkyl-substituted acrylamide, and N-vinyl-2-pyrrolidone. Examples of suitable lower alkyl-substituted acrylamides are methyl acrylamide, ethyl acrylamide, and t-butylacrylamide. The preferred C monomers are acrylic acid and acrylamide.

25 It is to be understood that the pressure-sensitive adhesive copolymer may comprise a single type of C monomer or may comprise two or more different C monomers.

The adhesive properties of the pressure-sensitive adhesive copolymer vary depending upon the particular combination and relative amounts of the A, B and C monomers employed in preparing the copolymer. The combination of types and amounts of A, B and C monomers is such that the adhesive and the adhesive-coated sheet material exhibit the indicated initial dry skin adhesion value, dry skin adhesion value after 48 hours, and moist skin adhesion value. Thus, any combination of types of A, B and C monomers may be employed so long as the resulting copolymer exhibits the required adhesion values. As to amounts, the



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5 B monomer is present in an amount of about 5 to 30% of the
total weight of all monomers in the copolymer and the C
monomer is present in an amount of about 0.5 to 30% of the
total weight of all monomers. The particular amounts of
the A, B and C monomers employed depend on the nature of
the A, B and C monomers selected. The amounts of the B and
C monomers may be varied within the above ranges so long as
the resulting adhesive copolymer exhibits the indicated
adhesion values. The amount of A monomer employed is
10 preferably about 50 to 95% by weight of the total weight of
all monomers in the copolymer, and is most preferably about
60 to 80% of the total weight of all monomers. Preferred
amounts for the B and C monomers are about 10 to 20% and
about 5 to 20%, respectively, based upon the total amount
15 of all monomers in the copolymer.

Copolymers containing solely A, B and C monomers
of appropriate types and in appropriate amounts perform
suitably in the practice of the invention. However, the
copolymers of the invention may further include minor
20 amounts of non-essential monomers such as methylacrylate,
ethylacrylate, vinylacetate and the like.

It may also be desirable in some instances in the
practice of the invention to increase internal strength or
cohesiveness of the copolymer by crosslinking the copolymer
25 using conventional methods (e.g., irradiation of the
copolymer or reaction of a crosslinking agent with reactive
functionality contained in the copolymer through inclusion
of a small amount of an appropriate monomer therein).

The pressure-sensitive adhesive copolymers may be
30 prepared using conventional free-radical-polymerization
methods. One particularly convenient method is the
following. The desired amounts of A, B and C monomers and
an organic solvent in which the monomers are soluble are
combined in a sealable bottle. A particularly suitable
35 solvent is ethyl acetate. A solvent such as isopropyl
alcohol which functions as a chain-transfer agent is also
present in the reaction medium in order to control the
molecular weight of the resulting adhesive copolymer. A
catalytic amount of a free-radical initiator such as



α, α' -azobisisobutyronitrile is then added to the solution. Nitrogen is bubbled through the solution to purge air from within the bottle, and the bottle is then sealed. The sealed bottle is tumbled in a heated water bath for a period of time sufficient to effect essentially complete polymerization. Generally, 24 hours has been found to be sufficient time to effect essentially complete polymerization when the water bath is maintained at about 55°C.

Backings which the pressure-sensitive adhesive of the invention may be coated onto or which the pressure-sensitive adhesive coated sheet materials of the invention may comprise include any of the well-known backings which find use in medical or surgical fields. Thus, the backing may be, for example, a conventional nonwoven fabric, woven fabric, knit, paper, or synthetic film backing. Preferred backings are nonwoven fabrics, woven fabrics, knits and the like which permit transpiration of perspiration and tissue or wound exudate therethrough.

The backing may be of any desired shape to provide adhesive coated sheet materials embodied as adhesive tapes, strips, wound dressings, monitoring or neuro-stimulating electrodes, drapes or the like.

The pressure-sensitive adhesive copolymer may be applied to the backing by conventional methods. As is known to those skilled in the art, the particular method selected may depend upon the nature of the backing being employed. For example, where the backing is a nonwoven fabric, a suitable method for applying the adhesive copolymer thereto involves coating a solution of the adhesive copolymer in an organic solvent onto a release liner, followed by lamination of the nonwoven fabric backing to the (semi-dry) adhesive coating.

TEST METHODS

The adhesive performance of the pressure-sensitive adhesive-coated sheet materials of the invention

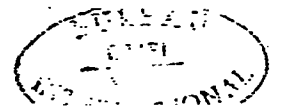


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is determined using the following Test Methods A, B and C:
Initial Dry Skin Adhesion (Test Method A)

The adhesive-coated sheet material to be tested is cut into 1x3 inch (2.5 x 7.6 cm) strips which are applied to the (dry) backs of each of 6 individuals (i.e., 3 men and 3 women, randomly selected) who are lying on procedure tables in prone positions with arms at the sides and heads turned to one side. For each individual, each of three strips of the sheet material is applied to one or the other side of the spinal column and is positioned such that the length of the strip is at right angles to the spinal column. The strips are applied without tension or pulling of the skin and there is at least a 1/8 to 3/8 inch space between each strip. After all strips are in place, a 4.5 pound rubber roller according to the specifications found in the 7th Edition of the Pressure-Sensitive Tape Council Brochure (1976), incorporated herein by reference, is rolled along the length of each strip, once in each direction, at a travel speed of about 3 inches per second, to assure even pressure application to each strip. When rolling the strip, no manual pressure should be applied to the roller.

To determine the adhesive value, each strip is removed at a 90° angle from a line formed by the spinal column using a conventional adhesion tester having a 25# test line and a 1-inch clip attached to the test line. The clip is attached to the edge of the strip which is farthest from the spinal cord, the clip being attached by manually lifting about 1/2-inch of that edge of the strip and attaching the clip thereto. This orientation permits the strip to be removed starting from the outside of the back towards the spine so that pull is with the direction of fine hair growth on the back. This is facilitated by positioning the adhesion tester opposite the side of the individual's back from which the strip is to be removed. The adhesion tester is aligned with and is at the same height as the strip to be removed in order to maintain the



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90° removal angle. The strip is pulled over itself in a plane parallel (180°) to the back and the rate of removal is 6 inches (15.2 cm) per minute. To determine initial skin adhesion, the strip is removed within about 5 minutes of its application to the back.

An acceptable sheet material in accordance with the invention exhibits an average initial dry skin adhesion value of at least about 0.75 Newton per 100 millimeters of width.

An example of a suitable adhesion tester for use in this Test Method A comprises a conventional motor driven screw with moving carriage and a transducer. Connected to the transducer is a load cell accessory. Removal force placed on the transducer results in a signal change which is passed through a readout meter to a strip chart recorder.

Dry Skin Adhesion After 48 Hours (Test Method B)

The adhesive-coated sheet material to be tested is cut into 1x3 inch (2.5 x 7.6 cm) strips which are applied to the (dry) backs of 6 individuals in accordance with the procedures of Test Method A above. Here, each strip is removed about 48 hours after its application. The procedure used for removal of the strip is that described in of Test Method A.

An acceptable sheet material in accordance with the invention exhibits an average dry skin adhesion value after 48 hours of no more than about 12 Newtons per 100 millimeters of width.

Moist Skin Adhesion (Test Method C)

Moist skin adhesion performance is determined utilizing a conventional constant temperature/humidity chamber such as that illustrated in FIGS. 1 and 2. The constant temperature/humidity chamber 10 comprises an insulated conditioning compartment 11 which serves as the constant temperature/humidity chamber in which the moist



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skin adhesion test is conducted, and compressor compartment 12 which houses the machinery that provides the proper conditions of temperature and humidity within conditioning compartment 11. Mounted externally on conditioning compartment 11 are control instruments 13 which maintain the proper conditions of temperature and humidity within conditioning compartment 11. Control instruments 13 include a recorder for recording the conditions of temperature and humidity over a period of time. Moisture is introduced into conditioning compartment 11 from an electrically-heated water reservoir (not illustrated) located within compressor compartment 12. Conditioning compartment 11 is fitted with door 14 which preferably comprises methylnmethacrylate or other transparent material. Door 14 contains two iris ports 15 and 16 which permit passage of bare arms therethrough into the constant temperature/humidity chamber. Conditioning chamber 11 also includes an adhesion tester 17 mounted on the exterior of wall 18 which is located opposite door 14, one suitable adhesion tester being that discussed above in connection with Test Method A. Test line 19 of adhesion tester 17 passes through channel 20 of wall 18. Water drain 21 functions to remove condensate from within conditioning compartment 11.

An example of a suitable commercially available constant temperature/humidity chamber which may be modified to include iris ports as described above is that available under the trade designation "TH-10" from Tenney Engineering, Inc., Union, N.J.

The following is a description of how moist skin adhesion is determined. Reference to the illustrated constant temperature/humidity chamber is for illustrative purposes only, it being understood that any type of constant temperature/humidity chamber may be used so long as it is capable of permitting the adhesion test to be performed under the indicated conditions of temperature and humidity.



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For the testing procedure, the chamber is equilibrated at approximately 100°F and 95% relative humidity. The individual, after moistening his or her forearm with tap water, places the forearm 22 in the chamber via iris port 15. After a few minutes have elapsed and an easily visible layer of moisture is present on the skin, a 1x3 inch (2.5 x 7.6 cm) strip 23 of the adhesive-coated sheet material to be tested is introduced into the chamber via iris port 16, and is applied to the inside, flat section of the forearm at a location about midway between the elbow and the wrist with the length of the strip parallel to the length of the arm (Fig. 1). The strip is secured with firm thumb pressure. After one minute of dwell time, the medial end of the strip is connected to a 1-inch clip 24 which in turn is connected through the test line 19 to the adhesion tester 17. While the forearm is held in a horizontal position with the strip facing up (Fig. 2), the strip is removed, at a 180° peel angle, parallel to the direction of the arm at a removal rate of 6 inches (15.2 cm) per minute.

For purposes of determining the moist skin adhesion value, three replicates of each strip are tested on each of 3 randomly selected individuals.

An acceptable sheet material in accordance with the invention exhibits an average moist skin adhesion value of at least about 2.2 Newtons per 100 millimeters of width.

Test Method D

The adhesion performance of the pressure-sensitive adhesives of the invention is determined by incorporating the particular pressure-sensitive adhesive in an adhesive-coated sheet material which is then tested in accordance with Test Methods A, B and C above. The adhesive-coated sheet material is prepared as follows:

A solution of the pressure-sensitive adhesive in an organic solvent is coated onto a silicone-treated release paper and allowed to air-dry at ambient conditions



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for about one minute. To the semi-dry adhesive layer is then laminated the web that is available commercially under the trade designation "916L" from Hollingsworth & Vose Co., East Walpole, Mass. This is a carded nonwoven web which is bonded with a latex binder. The resulting laminate is dried at 230°F (110°C.) until all solvent has evaporated (requiring about 5 minutes). The dried adhesive coating weight is about 700 mg/200 cm². The adhesive performance of the resulting adhesive-coated sheet material is then tested in accordance with Test Methods A, B and C above.

Inherent Viscosity Measurement

In order to understand the benefits derived from the teachings of this invention, it is necessary to relate the molecular weight of the copolymer to the dry and moist skin adhesion performance. The comparative molecular weights are determined by measuring the viscosity of dilute solutions of the adhesives prepared according to these teachings.

The inherent viscosity values which are reported in TABLES I and II of the Examples which follow were obtained by the conventional method used by those skilled in the art. The measurement of the viscosity of dilute solutions of the adhesive, when compared to controls run under the same conditions, clearly demonstrate the relative molecular weights. It is the comparative values which are significant and absolute figures are not required. In the examples, the inherent viscosity values were obtained using a Cannon-Fenske #50 viscometer in a water bath controlled at 25°C to measure the flow time of 10 ml of a polymer solution (0.2 g per deciliter polymer in tetrahydrofuran). The examples and controls being run for comparison were run under identical conditions. The test procedure followed and the apparatus used are explained in detail in the Textbook of Polymer Science, F. W. Billmeyer, Wiley-Interscience, 2nd Edition, 1971 under: Polymer chains and their characterization, D. Solution Viscosity and



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Molecular Size, pages 84 and 85.

EXAMPLES

The following detailed description includes exemplary preparations of various B monomers and various pressure-sensitive adhesive copolymers prepared with various A, B and C monomers.

B MONOMER PREPARATION

B monomers identified as "B-1" - "B-9" are prepared as follows:

MONOMER "B-1"

An acrylate ester of a polyether containing an average of about 7 repeating ethoxy units was prepared as follows:

To a 1000 ml round bottom flask fitted with a magnetic stirrer and a Dean Stark trap were added 144 g (0.4 m) of Carbowax® 350 (a methoxy poly(ethylene oxide) ethanol of about 350 MW, available from Union Carbide Corp.) 36 g (0.5 m) of acrylic acid, 9.6 g of p-toluene-sulfonic acid, 0.15 g of phenothiazine, and 160 g of toluene. The mixture was refluxed, with stirring and under a nitrogen stream, for 16 hours, during which time about 9 ml of water were collected in the Dean Stark trap. The mixture was cooled to room temperature, and 10.5 g of calcium hydroxide was added thereto. The mixture was stirred for 2 hours, after which time it was filtered through "Super Cel" (a highly pure amorphous diatomaceous silica, available from Johns-Manville, Celite Division). The filtrate thereby obtained was subjected to rotary evaporation to provide 164.2 g (98.2% yield) of a solid material which was used for preparing pressure-sensitive adhesive copolymers of the invention. This solid was then used to prepare copolymers as described in the examples which follow.



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MONOMER "B-2"

An acrylate ester of a polyether containing an average of about 12 repeating ethoxy units was prepared as follows.

5 To a flask of the type described above were added 211.2 g (0.4 m) of Carbowax® 550 (a methoxy poly(ethylene oxide) ethanol of approximately 550 MW, available from Union Carbide Corp.) and 211.2 g of toluene. The mixture was refluxed under a nitrogen stream for 1.5 hours to
10 remove dissolved oxygen. To this solution was then added 33.8 g (0.5 m) of acrylic acid, 0.16 g of copper powder and 9.2 g of p-toluenesulfonic acid. The resulting mixture was refluxed, with stirring and under a nitrogen stream, for 16 hours with generated water being collected in the Dean
15 Stark trap. The mixture was cooled to room temperature and 10 g of calcium hydroxide was added thereto. The mixture was stirred for 2 hours and then filtered through "Super Cel". The monomethyl ether of hydroquinone, 0.5 g, was added to the filtrate and the solvent was removed by rotary
20 evaporation to provide a white solid. This solid was then used to prepare copolymers as described in the examples which follow.

MONOMER "B-3"

25 An acrylate ester of a polyether containing an average of about 16 repeating ethoxy units was prepared as follows.

Two hundred eighty-eight g (0.4 m) of Carbowax®
750 (a methoxy poly(ethylene oxide) ethanol of
30 approximately 750 MW, available from Union Carbide Corp.) was melted in a flask of the type described above. Toluene, 288 g, was added to the flask and the solution was refluxed, with stirring and under a nitrogen stream, for 2 hours. To this solution was then added 33.8 g (0.5 m) of
35 acrylic acid, 9.2 g of p-toluenesulfonic acid, and 0.16 g of copper powder. The resulting mixture was then refluxed, treated with calcium hydroxide, and filtered, all in



accordance with the procedure for preparing Monomer "B-2" above. To the pale yellow filtrate thereby obtained was added 0.06 g of monomethyl ether of hydroquinone. Aliquots of this filtrate were then used to prepare certain copolymers as described in the examples which follow.

In some instances, Monomer "B-3" was also prepared by following the above procedure, except that here the monomer was isolated from the solvent by rotary evaporation as described in connection with the preparation of monomer "B-2". This solid was then used to prepare certain copolymers as described in the examples which follow.

MONOMER "B-4"

A methacrylate ester of a polyether containing an average of about 16 repeating ethoxy units was prepared as follows.

Two hundred eighty eight g (0.4 m) of Carbowax® 750 was melted in a flask of the type described above. Toluene, 288 g, was then added to the flask and the resulting solution was refluxed, with stirring and under a nitrogen stream, for 1.5 hours. To this solution was added 40.4 g (0.5 m) of methacrylic acid, 9.2 g of p-toluenesulfonic acid and 0.16 g of copper powder. The resulting mixture was then refluxed, treated with calcium hydroxide and filtered, all in accordance with the procedure for preparing Monomer "B-2" above. To the pale yellow filtrate thereby obtained was added 0.08 g of monomethyl ether of hydroquinone. Aliquots of this filtrate were then used to prepare copolymers as described in the examples which follow.

MONOMER "B-5"

An acrylate ester of a polyether containing an average of about 45 repeating ethoxy units was prepared as follows.



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To a flask of the type described above were added 144 g (0.072 m) of Carbowax® 2000 (a methoxy poly(ethylene oxide) ethanol of about 2000 MW, available from Union Carbide Corp.), 20 g (0.3 m) of acrylic acid, 6 g of p-toluenesulfonic acid, 0.1 g of phenothiazine, and 160 g of toluene. The mixture was refluxed, with stirring and under nitrogen stream, for 16 hours with generated water being collected in the Dean Stark trap. The mixture was cooled to 40°C. Ten g of calcium hydroxide was then added and the mixture was stirred for 2 hours. After warming to 40°C, the mixture was filtered through "Super Cel" and added dropwise to 2 liters of heptane to provide a white powder. This powder was then used to prepare copolymers as described in the example, which follow.

MONOMER "B-6"

An acrylate ester of a polyether containing an average of about 114 repeating ethoxy units was prepared as follows.

To a flask of the type described above were added 144 g (0.03 m) of Carbowax® 5000 (a methoxy poly(ethylene oxide) ethanol of about 5000 MW, available from Union Carbide Corp.), 20 g (0.3 m) of acrylic acid, 6 g of p-toluenesulfonic acid, 0.1 g of phenothiazine, and 160 g of toluene. The resulting mixture was refluxed, treated with calcium hydroxide and filtered, and the resulting filtrate was added to heptane, all in accordance with the procedure for preparing Monomer "B-5" above except that here 6.5 g of calcium hydroxide was employed instead of the indicated 10 g. The resulting powder was then used to prepare copolymers as described in the examples which follow.

MONOMER "B-7"

An acrylate ester of a polyether containing an average of about 17 repeating propoxy units was prepared as follows.



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To a flask of the type described above were added 205.4 g (0.2 m) of UCON® LB 285 (an n-butoxy poly(propylene oxide) propanol of about 1000 MW, available from Union Carbide Corp.), 24.1 g (0.3 m) of acrylic acid, 6.6 g of p-toluenesulfonic acid, 0.72 g of copper powder, and 288 g of toluene. The mixture was refluxed, with stirring and under a nitrogen stream, for 16 hours, during which period about 3.5 ml of water was collected in the Dean Stark trap. The mixture was then cooled to room temperature, and 7.2 g of calcium hydroxide was added thereto. The resulting cloudy white mixture was stirred for 1 hour at room temperature, during which time it turned pale blue. An additional 2 g of calcium hydroxide was added with no change in color observed, and the mixture was stirred another 1-1/2 hours. The mixture was filtered through "Super Cel" to provide a clear emerald green filtrate to which was added 0.09 g of monomethyl ether of hydroquinone. After storing under refrigeration for two days, the filtrate was passed through an column containing Amberlite® IR-120 ion exchange resin (available from Rohm and Haas) which has been previously treated with sulfuric acid. Sufficient solvent was removed from the pale yellow filtrate thereby obtained to provide a 91.5% solids solution. Aliquots of this solution were then used to prepare copolymers as described in the examples which follow.

MONOMER "B-8"

An acrylate ester of a polyether containing an average of about 20 repeating ethoxy/propoxy units was prepared as follows.

To a flask of the type described above were added 208.4 g of (0.2 m) of UCON® 50-HB260 (an n-butoxy poly(ethylene oxide/propylene oxide) [50:50 by weight] alcohol of about 1000 MW, available from Union Carbide Corp.), 24.5 g (0.3 m) of acrylic acid, 6.7 g of p-toluenesulfonic acid, 0.73 g of copper powder and 288 g



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of toluene. The mixture was refluxed, with stirring and under a nitrogen stream, for 16 hours during which period about 4 ml of water was collected in the Dean Stark trap. The mixture was then cooled to room temperature, and 7.3 g of calcium hydroxide was added thereto. The cloudy white solution was stirred for 2 hours at room temperature, and was then filtered through "Super Cel" to provide 454 g of a clear light green filtrate. Monomethyl ether of hydroquinone, 0.09 g, was added to the filtrate which was then stored under refrigeration for 3 days. The filtrate was subsequently passed through a column containing 10 g of Amberlite® IR-120 ion exchange resin (available from Rohm and Haas) which has been previously treated with sulfuric acid. Sufficient solvent was removed from the pale yellow filtrate thereby obtained to provide a 92.7% solids solution. Aliquots of this solution were then used to prepare copolymers as described in the examples which follow.

MONOMER "B-9"

An acrylate ester of a polyether containing an average of about 222 repeating tetramethylene oxide units was prepared as follows.

To a flame-dried 1000 ml 3-neck flask equipped with a condensor, thermometer and nitrogen inlet were added 300 g of tetrahydrofuran and 52 g of cyclohexane, and the resulting mixture was cooled to about 10°C by placing the flask in an ice-water bath. Methyl trifluoromethyl-sulfonate, 4.9 g, was added to the cooled mixture using a dry syringe. The mixture was then allowed to warm to 20 ± 4°C, and was maintained at that temperature for about 5-1/2 hours.

The polytetrahydrofuran polymer-containing mixture obtained above was added to a mixture of 2.2 g (0.02987 m) of acrylic acid, 2.9 g of anhydrous ammonium carbonate and 80 g of ethanol. The mixture was stirred overnight, after which time 300 g of the hydroxy form of



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Amberlite® IR-402 (available from Rohm & Haas) was added thereto. The mixture was then filtered using a Buchner funnel and No. 4 Whatman filter paper. The resulting filtrate was concentrated to about 70% solids using rotary evaporation. To the solution thereby obtained was added 0.2 g of phenothiazine, and the solution was then dried in an oven to provide a solid which was used to prepare copolymers as described in the Examples which follow.

10

EXAMPLES 1-45

Pressure-sensitive adhesive copolymers of the invention which comprised the indicated A, B, and C monomers in the indicated amounts (TABLE I) were prepared as follows:

15

To a 4 ounce glass bottle were added the indicated amounts (by weight) of the indicated A, B and C monomers; an amount (by weight) of the indicated solvent blend which provided a solution which was either 40% solids by weight (Examples 29, 30 and 33) or 50% solids by weight (Examples 1-28, 31-32 and 34-45); and α, α' -azobis-isobutyronitrile in an amount of either 0.2% by weight (Examples 1-7 and 24) or 0.3% by weight (Examples 8-23 and 25-45) based on the total weight of the A, B and C monomers and the solvent blend. As indicated above, Monomers "B-4", "B-7", and "B-8" were added to the other ingredients of the various reaction mixtures as solutions in toluene, thereby introducing the indicated amounts of toluene into those reaction mixtures containing those B monomers. This was also the case where indicated for Monomer "B-3". In all other cases, the reaction medium contained only ethyl acetate and isopropanol. The bottle was purged to eliminate air therefrom by bubbling nitrogen through the solution. The bottle was then sealed, and was tumbled for 24 hours in a water bath maintained at 55°C. The solution of the respective pressure-sensitive adhesive copolymer was then coated onto a backing as described below.

30

35



Adhesive-coated sheet materials of the invention which comprise the various pressure-sensitive adhesive copolymers prepared above (and described in TABLE I) were prepared as follows:

5 The solution of the respective pressure-sensitive adhesive copolymer was coated onto a silicone-treated release paper and allowed to air-dry for one minute under ambient conditions. A conventional nonwoven web of rayon staple fibers bonded with an acrylic latex binder was then
10 laminated to the semi-dry adhesive coating. The resulting laminate was dried at 230°F. until all solvent had evaporated. The dried adhesive coating weight was about 700 mg/200 cm².

15 The resulting adhesive-coated sheet materials of the invention were tested in accordance with Test Methods A, B and C above and the results observed are listed in TABLE I. All of these adhesive-coated sheet materials were suitable in terms of initial dry skin adhesion performance, dry skin adhesion performance after 48 hours, and moist
20 skin adhesion performance, and no irritation of skin was observed. TABLE I also lists the inherent viscosity (determined as described above) for each copolymer.

TABLE I

| Example | Copolymer Composition | | | Monomer Ratio (% by weight) | | | Solvent Ratio (% by weight) | | | Adhesive Performance Newtons per 100 mm width | | | |
|---------|-----------------------|--------------------------------|----|--------------------------------|----|----|--------------------------------|--------|---------|--|---------------------------|---------------------------|-------------------|
| | Monomer | | | Monomer | | | | | | Dry Skin | | | |
| | | | | | | | | | | | | | |
| | | | | | | | | | | | | | |
| | A | B | C | A | B | C | EtOAc | i-PrOH | Toluene | Inherent Viscosity | Initial Dry Skin Adhesion | Moist After Skin Adhesion | 48 Hours Adhesion |
| 1 | IOA | EOA ₂ ^a | AA | 90 | 5 | 5 | 90 | 10 | 0 | 0.69 | 9.2 | 8.6 | 3.7 |
| 10 2 | IOA | EOA ₂ ^a | AA | 80 | 10 | 10 | 83 | 17 | 0 | 0.68 | 3.8 | 6.6 | 5.0 |
| 3 | IOA | "B-1" | AA | 80 | 5 | 15 | 81 | 19 | 0 | 0.73 | 1.2 | 2.3 | 3.6 |
| 4 | IOA | "B-1" | AA | 80 | 10 | 10 | 77 | 23 | 0 | 0.76 | 5.4 | 4.7 | 3.1 |
| 5 | IOA | "B-1" | AA | 70 | 10 | 20 | 72 | 28 | 0 | 0.86 | 1.0 | 2.6 | 3.8 |
| 6 | IOA | "B-1" | AA | 70 | 20 | 10 | 58 | 42 | 0 | 0.76 | 4.3 | 3.8 | 2.4 |
| 15 7 | IOA | "B-1" | AA | 60 | 20 | 20 | 48 | 52 | 0 | 0.75 | 0.8 | 1.2 | 3.7 |
| 8 | IOA | EOA ₁₀ ^b | AA | 80 | 10 | 10 | 85 | 15 | 0 | 0.73 | 4.8 | 6.9 | 5.8 |

TABLE I

| Example | Copolymer Composition | | | Monomer Ratio (% by weight) | | | Solvent Ratio (% by weight) | | | Adhesive Performance Newtons per 100 mm width | | | |
|---------|-----------------------|-------|----|--------------------------------|----|----|--------------------------------|--------|---------|--|---------------------------|----------------------------------|---------------------|
| | Monomer | | | Monomer | | | | | | | | | |
| | A | B | C | A | B | C | EtOAc | i-PrOH | Toluene | Inherent Viscosity | Initial Dry Skin Adhesion | Dry Skin Adhesion After 48 Hours | Moist Skin Adhesion |
| | | | | | | | | | | | | | |
| | | | | | | | | | | | | | |
| 9 | IOA | "B-2" | AA | 70 | 20 | 10 | 80 | 20 | 0 | 0.73 | 7.0 | 4.9 | 2.6 |
| 10 | IOA | "B-3" | AA | 90 | 5 | 5 | 90 | 10 | 0 | 0.86 | 9.8 | 6.3 | 2.5 |
| 11 | IOA | "B-3" | AA | 80 | 5 | 15 | 85 | 15 | 0 | 0.77 | 1.8 | 4.5 | 2.4 |
| 10-12 | IOA | "B-3" | AA | 73 | 10 | 17 | 83 | 17 | 0 | 0.71 | 1.1 | 3.6 | 4.6 |
| 13 | IOA | "B-3" | AA | 73 | 15 | 12 | 83 | 17 | 0 | 0.70 | 4.0 | 7.1 | 3.5 |
| 14 | IOA | "B-3" | AA | 70 | 15 | 15 | 75 | 25 | 0 | 0.85 | 2.9 | 5.9 | 4.5 |
| 15 | IOA | "B-3" | AA | 70 | 10 | 20 | 85 | 15 | 0 | 0.79 | 1.1 | 2.7 | 4.1 |
| 16 | IOA | "B-3" | AA | 70 | 20 | 10 | 72 | 28 | 0 | 0.68 | 5.2 | 4.0 | 2.4 |

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TABLE I

| Example | Copolymer Composition | | | Monomer Ratio (% by weight) | | | Solvent Ratio (% by weight) | | | Adhesive Performance Newtons per 100 mm width | | | |
|---------|-----------------------|--------------------------------|----|--------------------------------|----|----|--------------------------------|--------|---------|--|----------------------------|---------------------------|---------------------|
| | Monomer | | | Monomer | | | | | | Dry Skin | | | |
| | | | | | | | | | | | | | |
| | | | | | | | | | | | | | |
| | A | B | C | A | B | C | EtOAc | i-PrOH | Toluene | Inherent Viscosity | Dry Skin Adhesion 48 Hours | Initial Dry Skin Adhesion | Moist Skin Adhesion |
| 17 | IOA | "B-3" | AA | 68 | 19 | 13 | 80 | 20 | 0 | 0.70 | 7.4 | 5.4 | 4.3 |
| 18 | IOA | "B-3" | AA | 66 | 17 | 17 | 80 | 20 | 0 | 0.77 | 4.0 | 1.3 | 3.0 |
| 19 | IOA | "B-3" | AA | 60 | 20 | 20 | 60 | 40 | 0 | 0.63 | 4.4 | 1.5 | 3.7 |
| 20 | IOA | "B-3" | AA | 50 | 25 | 25 | 65 | 35 | 0 | 0.61 | 3.8 | 1.4 | 6.8 |
| 21 | IOA | EOMA ^c ₅ | AA | 70 | 15 | 15 | 85 | 15 | 0 | 0.79 | 2.4 | 0.8 | 3.8 |
| 22 | IOA | EOMA ^c ₅ | AA | 80 | 10 | 10 | 90 | 10 | 0 | 0.83 | 4.2 | 1.6 | 3.5 |
| 23 | IOA | EOMA ^d ₉ | AA | 80 | 10 | 10 | 80 | 20 | 0 | 0.85 | 4.1 | 3.6 | 2.3 |
| 24 | IOA | "B-9" | AA | 80 | 10 | 10 | 90 | 10 | 0 | 0.81 | 3.5 | 1.7 | 6.3 |

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TABLE I

| Adhesive Performance | | | | | | | | | | | | | | | | |
|--------------------------|-----------------------|--------------------------------|----|----|----|----|---------------|----|------|---------------|--------|---------|--------------------|----------|------------------|------------|
| Newtons per 100 mm width | | | | | | | | | | | | | | | | |
| Example | Copolymer Composition | | | | | | Monomer Ratio | | | Solvent Ratio | | | | | | |
| | Monomer | | | | | | (% by weight) | | | (% by weight) | | | | | | |
| | Monomer | | | | | | | | | | | | | | | |
| | Monomer | | | | | | | | | | | | | | | |
| | A | B | C | A | B | C | A | B | C | EtOAc | i-PrOH | Toluene | Inherent Viscosity | Dry Skin | Initial Adhesion | Moist Skin |
| 25 | IOA | "B-5" | AA | 70 | 15 | 15 | 40 | 60 | 0 | 0.74 | 2.1 | 5.7 | 4.6 | | | |
| 26 | IOA | "B-6" | AA | 70 | 15 | 15 | 65 | 35 | 0 | 0.72 | 1.7 | 5.0 | 3.0 | | | |
| 27 | IOA | "B-8" | AA | 70 | 15 | 15 | 85 | 15 | 0 | 0.90 | 1.3 | 5.2 | 8.4 | | | |
| 28 | IOA | "B-7" | AA | 70 | 15 | 15 | 70 | 30 | 0 | 0.76 | 1.2 | 2.7 | 4.2 | | | |
| 29 | IOA | EGMA ^e ₅ | AA | 70 | 15 | 15 | 40 | 60 | 0 | 0.66 | 1.8 | 4.0 | 5.1 | | | |
| 30 | IOA | "B-4" | AA | 70 | 15 | 15 | 47.5 | 45 | 7.5 | 0.70 | 3.5 | 5.1 | 6.6 | | | |
| 31 | 2EHA | "B-3" | AA | 70 | 15 | 15 | 85 | 15 | 0 | 0.84 | 1.4 | 6.3 | 6.3 | | | |
| 32 | n-BA | "B-3" | AA | 70 | 15 | 15 | 28.2 | 60 | 11.8 | 0.76 | 2.2 | 4.7 | 3.6 | | | |

10

15



TABLE I

| 5 | Adhesive Performance | | | | | | | | | | | | |
|---------|--------------------------|-------|------|---------------|----|---------------|-------|--------|---------|--------------------|---------------------------|-------------------------|---------------------|
| | Newtons per 100 mm width | | | | | | | | | | | | |
| | Monomer Ratio | | | | | Dry Skin | | | | | | | |
| | Copolymer Composition | | | (% by weight) | | Solvent Ratio | | | | | | | |
| | Monomer | | | Monomer | | (% by weight) | | | | | | | |
| Example | A | B | C | A | B | C | EtOAc | i-PrOH | Toluene | Inherent Viscosity | Initial Dry Skin Adhesion | After 48 Hours Adhesion | Moist Skin Adhesion |
| 33 | IOA:nBA | "B-3" | AA | 35:35 | 15 | 15 | 70 | 30 | 0 | 0.75 | 2.0 | 3.2 | 3.4 |
| 34 | IMA | "B-3" | AA | 70 | 20 | 10 | 50 | 50 | 0 | 0.68 | 3.9 | 7.5 | 2.6 |
| 35 | IOA | "B-3" | MAA | 70 | 15 | 15 | 75 | 25 | 0 | 0.89 | 0.85 | 3.2 | 2.3 |
| 36 | IOA | "B-3" | MAA | 80 | 15 | 5 | 53.2 | 35 | 11.8 | 0.65 | 5.3 | 4.5 | 3.3 |
| 37 | IOA | "B-3" | MACM | 85 | 10 | 5 | 90 | 10 | 0 | 0.80 | 2.6 | 7.1 | 2.3 |
| 38 | IOA | "B-3" | ACM | 79 | 15 | 6 | 90 | 10 | 0 | 0.90 | 1.6 | 6.3 | 2.8 |
| 39 | IOA | "B-3" | ACM | 82 | 15 | 3 | 90 | 10 | 0 | 0.91 | 6.6 | 5.6 | 2.8 |
| 40 | IOA | "B-3" | ACM | 94 | 5 | 1 | 92 | 8 | 0 | 0.69 | 1.7 | 0.7 | 2.4 |

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TABLE I

| TABLE I | | | | | | | | | | | | | | | | |
|---------|-----------------------|----------|----------|---------|------|----------|--------------------------------|----|------|--------------------------------|--------|--|-----------------------|----------|--|--|
| Example | Copolymer Composition | | | | | | Monomer Ratio (% by weight) | | | Solvent Ratio (% by weight) | | Adhesive Performance Newtons per 100 mm width | | | | |
| | Monomer | | | Monomer | | | Monomer | | | EtOAc | i-PrOH | Toluene | Inherent Viscosity | Dry Skin | | |
| | A | B | C | A | B | C | A | B | C | | | | | | | |
| | | | | | | | | | | | | | | | | |
| | Initial | Dry Skin | Adhesion | Moist | Skin | Adhesion | | | | | | | | | | |
| 41 | IOA | "B-3" | t-BAM | 80 | 15 | 5 | 53.2 | 35 | 11.8 | 0.73 | 2.0 | 1.3 | 3.4 | | | |
| 42 | IOA | "B-3" | ACM | 89 | 8 | 3 | 92 | 8 | 0 | 0.83 | 8.6 | 8.2 | 5.9 | | | |
| 43 | IOA | "B-3" | ACM | 85 | 10 | 5 | 90 | 10 | 0 | 0.80 | 7.2 | 10.4 | 5.4 | | | |
| 44 | IOA | "B-3" | ITAC | 80 | 15 | 5 | 41.7 | 45 | 13.3 | 0.68 | 4.3 | 3.9 | 4.4 | | | |
| 45 | IOA | "B-3" | NVP | 60 | 10 | 30 | 85 | 15 | 0 | 0.90 | 2.4 | 11.7 | 3.7 | | | |



- a the 2-(2-ethoxyethoxy)ethyl acrylate which is available under the trade designation "SR-256" from Sartomer Company, West Chester, PA
- b the methoxy poly(ethylene oxide) acrylate which is available under the trade designation "No. 8816" from Monomer-Polymer & Dajac Laboratories, Inc., Trevoise, PA
- c the methoxy poly(ethylene oxide) methacrylate of 200 Daltons which is available under the trade designation "No. 16664" from Polysciences, Inc., Warrington, PA
- d the methoxy poly(ethylene oxide) methacrylate of 400 Daltons which is available under the trade designation "No. 16665 from Polysciences, Inc., Warrington, PA
- e the hydroxy poly(ethylene oxide)₅ methacrylate which is available under the trade designation "No. 16712" from Polysciences, Inc., Warrington, PA

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Abbreviations:

| | |
|--------------------------|-----------------------------|
| IOA = isooctylacrylate | t-BAM = t-butylacryamide |
| AA = acrylic acid | ACM = acrylamide |
| n-BA = n-butylacrylate | ITAC = itaconic acid |
| LMA = laurylmethacrylate | NVP = N-vinyl-2-pyrrolidone |
| MAA = methacrylic acid | 2EHA = 2-ethylhexylacrylate |
| MACM = methacrylamide | |



COMPARATIVE EXAMPLES 46-74

Pressure-sensitive adhesive copolymers comprising the indicated A and C monomers or the indicated A, B, and C monomers in the indicated amounts (TABLE II) were prepared as follows:

To a 4 ounce glass bottle were added the indicated amounts (by weight) of the A and C monomers, or A, B and C monomers; an amount (by weight) of the indicated solvent blend which provided a solution which was either 40% solids by weight (Example 70) or 50% solids by weight (Examples 46-69 and 71-74); and α, α' -azobisisobutyronitrile in an amount of either 0.2% by weight (Examples 48-52) or 0.3% by weight (Examples 46-47 and 53-74). Again, in some cases as indicated, Monomer "B-3" was added to the other ingredients of the reaction mixture as a solution in toluene, thereby introducing the indicated amount of toluene into those reaction mixtures containing Monomer "B-3". The bottle was then purged, sealed and tumbled as described in Examples 1-45 to provide a solution of each respective copolymer.

Each respective copolymer was applied to the nonwoven web of the type described in Examples 1-45 in accordance with the procedures of Examples 1-45.

The resulting copolymer-coated sheet materials were tested in accordance with Test Methods A, B and C and the results observed are listed in TABLE II. TABLE II also lists the inherent viscosity (determined as described above) for each copolymer.



TABLE II

| Example | <u>Copolymer Composition</u> | | | <u>Monomer Ratio</u> (% by weight) | | | <u>Solvent Ratio</u> (% by weight) | | | <u>Adhesive Performance</u> Newtons per 100 mm width | | | | |
|---------|------------------------------|-----|-------|---------------------------------------|----|----|---------------------------------------|--------|---------|---|----------------------------|---------------------------------|-----|-----|
| | <u>Monomer</u> | | | <u>Monomer</u> | | | | | | | | | | |
| | A | B | C | A | B | C | EtOAc | i-PrOH | Toluene | Inherent Viscosity | Dry Skin Adhesion 48 Hours | Moist Skin Adhesion 48 Hours | | |
| | | | | | | | | | | | | | | |
| | | | | | | | | | | | | | | |
| 5 | 46 | IOA | -- | AA | 90 | -- | 10 | 93 | 7 | 0 | 0.85 | 1.9 | 4.0 | 2.0 |
| | 47 | IOA | -- | AA | 80 | -- | 20 | 90 | 10 | 0 | 0.82 | 0 | 0 | 1.0 |
| 10 | 48 | IOA | "B-1" | -- | 90 | 10 | -- | 83 | 17 | 0 | 0.74 | extremely low internal strength | | |
| | 49 | IOA | "B-1" | -- | 80 | 20 | -- | 72 | 28 | 0 | 0.91 | extremely low internal strength | | |
| | 50 | IOA | "B-1" | AA | 90 | 5 | 5 | 86 | 14 | 0 | 0.72 | 4.6 | 2.9 | 1.1 |

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TABLE II

| Example | Copolymer Composition | | | Monomer Ratio (% by weight) | | | Solvent Ratio (% by weight) | | | Adhesive Performance Newtons per 100 mm width | | | |
|---------|-----------------------|-----------------------------------|---|--------------------------------|----|----|--------------------------------|--------|---------|--|---------------------------|---------------------|--|
| | Monomer | | | Monomer | | | | | | Dry Skin | | | |
| | | | | | | | | | | | | | |
| | | | | | | | | | | | | | |
| | A | B | C | A | B | C | EtOAc | i-PrOH | Toluene | Inherent Viscosity | Initial Dry Skin Adhesion | After Skin Adhesion | Moist Skin Adhesion |
| 5 | | | | | | | | | | | | | |
| 51 | IOA | "B-1" AA | | 80 | 15 | 5 | 72 | 28 | 0 | 0.76 | 3.4 | 1.8 | 1.1 |
| 52 | IOA | "B-1" AA | | 70 | 15 | 15 | 63 | 37 | 0 | 0.76 | 2.2 | 3.4 | 1.5 |
| 10 | IOA | EOA ₁₀ ^a AA | | 70 | 10 | 20 | 85 | 15 | 0 | 1.10 | no adhesion to dry skin | | 6.1 |
| 54 | IOA | EOA ₁₀ ^a AA | | 70 | 23 | 7 | 75 | 25 | 0 | 0.63 | 3.1 | 5.3 | extremely soft and stringy on moist skin |
| 15 | IOA | EOA ₁₀ ^a AA | | 60 | 20 | 20 | 70 | 30 | 0 | 0.77 | 0.6 | 1.2 | 6.0 |
| 56 | IOA | "B-2" AA | | 90 | 5 | 5 | 92 | 8 | 0 | 0.88 | 9.5 | 5.1 | 2.1 |

TABLE II

| 5 | Adhesive Performance | | | | | | | | | |
|---------|--------------------------|-------|----|-----------------------------|----|----|-----------------------------|--------|---------|-------------------|
| | Newtons per 100 mm width | | | | | | | | | |
| | Dry Skin | | | | | | | | | |
| | Initial Adhesion Moist | | | | | | | | | |
| | Inherent Viscosity | | | | | | | | | |
| Example | Copolymer Composition | | | Monomer Ratio (% by weight) | | | Solvent Ratio (% by weight) | | | Adhesion 48 Hours |
| | Monomer | | | Monomer | | | Monomer | | | Adhesion |
| | A | B | C | A | B | C | EtOAc | i-PrOH | Toluene | |
| 57 | IOA | "B-2" | AA | 80 | 10 | 10 | 83 | 17 | 0 | 3.0 4.5 1.9 |
| 58 | IOA | "B-2" | AA | 80 | 15 | 5 | 85 | 15 | 0 | 3.8 2.4 1.8 |
| 59 | IOA | "B-2" | AA | 80 | 5 | 15 | 87 | 13 | 0 | 2.3 3.6 2.0 |
| 60 | IOA | "B-2" | -- | 80 | 20 | -- | 86 | 14 | 0 | 0.8 0.3 1.3 |
| 61 | IOA | "B-2" | AA | 70 | 10 | 20 | 81 | 19 | 0 | 0.7 1.6 4.0 |
| 62 | IOA | "B-2" | AA | 70 | 15 | 15 | 78 | 22 | 0 | 2.6 3.6 1.9 |
| 63 | IOA | "B-2" | AA | 60 | 20 | 20 | 70 | 30 | 0 | 1.9 2.1 2.0 |
| 64 | IOA | "B-3" | AA | 80 | 10 | 10 | 80 | 20 | 0 | 4.1 4.2 1.9 |

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TABLE II

| Adhesive Performance | | | | | | | | | | | | | | | | | |
|--------------------------|-----------------------|------|--------------------------------|---------|----|----|--------------------------------|----|----|--------------------------------|--------|-----------------------------------|--------------------|-------------------------|---------------------|--|--|
| Newtons per 100 mm width | | | | | | | | | | | | | | | | | |
| Example | Copolymer Composition | | | | | | Monomer Ratio (% by weight) | | | Solvent Ratio (% by weight) | | | Dry Skin | | | | |
| | Monomer | | | Monomer | | | Monomer | | | | | | Initial Adhesion | | | | |
| | A | B | C | A | B | C | A | B | C | EtOAc | i-PrOH | Toluene | Inherent Viscosity | Dry Skin After 48 Hours | Moist Skin Adhesion | | |
| | | | | | | | | | | | | | | | | | |
| | | | | | | | | | | | | | | | | | |
| 5 | 65 | IOA | "B-3" | AA | 80 | 15 | 5 | 82 | 18 | 0 | 0.84 | 5.2 | 4.7 | 2.1 | | | |
| | 66 | IOA | EOA ^b ₂₂ | AA | 70 | 15 | 15 | 83 | 17 | 0 | 0.97 | 1.6 | 2.8 | 1.0 | | | |
| 10 | 67 | IOA | EOA ^b ₂₂ | AA | 80 | 10 | 10 | 88 | 12 | 0 | 0.99 | 3.8 | 4.9 | 0.6 | | | |
| | 68 | IOA | EOA ^c ₉ | AA | 70 | 15 | 15 | 65 | 35 | 0 | 0.78 | 1.4 | 2.8 | 2.0 | | | |
| | 69 | i-BA | "B-3" | -- | 95 | 5 | -- | 90 | 10 | 0 | 0.84 | 6.8 | 7.2 | 1.2 | | | |
| | 70 | MA | "B-3" | AA | 70 | 15 | 15 | 65 | 35 | 0 | 0.74 | not a pressure-sensitive adhesive | | | | | |
| 15 | 71 | n-BA | "B-3" | AA | 73 | 15 | 12 | 28 | 60 | 12 | 0.70 | 3.7 | 7.7 | 1.5 | | | |

TABLE II

| 5 | Adhesive Performance | | | | | | | | | |
|---------|--------------------------|-------|-----------------------------|----|----|-----------------------------|-------|--------------------|-------------------|------------------------------------|
| | Newtons per 100 mm width | | | | | | | | | |
| | Dry Skin | | | | | | | | | |
| | Initial Adhesion Moist | | | | | | | | | |
| | Dry Skin After Skin | | | | | | | | | |
| Example | Copolymer Composition | | Monomer Ratio (% by weight) | | | Solvent Ratio (% by weight) | | Inherent Viscosity | Adhesion 48 Hours | |
| | Monomer | | Monomer | | | | | | | |
| | A | B | C | A | B | C | EtOAc | i-PrOH | Toluene | |
| 72 | IOA | "B-3" | ITAC | 80 | 10 | 10 | 92 | 8 | 0 | 1.6 6.2 1.1 |
| 73 | IOA | "B-3" | VOAC | 65 | 15 | 20 | 48 | 40 | 12 | extremely soft and stringy polymer |
| 74 | IOA | "B-3" | VOAC | 75 | 15 | 10 | 53 | 35 | 12 | 0.72 |

10



WHAT IS CLAIMED IS:

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1. A normally tacky and pressure-sensitive adhesive coated sheet material having a backing member and a coating covering at least a portion of one major surface thereof of a pressure-sensitive adhesive composition comprising a copolymer consisting essentially of copolymerized A, B and C monomers as follows:

A is a hydrophobic monomeric acrylic acid ester of a non-tertiary alcohol, said alcohol having from 4 to about 14 carbon atoms;

B is a hydrophilic monomer which has a vinyl group copolymerizable with said A monomer and is other than acrylic acid, methacrylic acid, itaconic acid, acrylamide, methacrylamide, lower alkyl-substituted acrylamide, and N-vinyl-2-pyrrolidone, the amount by weight of B monomer being about 5 to 30% of the total weight of all monomers in the copolymer; and

C is at least one polar monomer copolymerizable with said A and B monomers, selected from the group consisting of acrylic acid, methacrylic acid, itaconic acid, acrylamide, methacrylamide, lower alkyl-substituted acrylamide, and N-vinyl-2-pyrrolidone, the amount of weight of C monomer being about 0.5 to 30% of the total weight of all monomers in the copolymer;

wherein said A, B and C monomers are copolymerized to form a polymeric backbone and the combination of A, B and C monomers being such as to provide said sheet material with an initial dry skin adhesion of at least about 0.75 Newton per 100 millimeters of width, a dry skin adhesion value after 48 hours of not more than about 12 Newtons per 100 millimeters of width, and a moist skin adhesion value of at least about 2.2 Newtons per 100 millimeters of width.



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2. A normally tacky and pressure sensitive adhesive comprising a copolymer consisting essentially of copolymerized A, B and C monomers as follows:

5 A is a hydrophobic monomeric acrylic acid ester of a non-tertiary alcohol, said alcohol having from 4 to 14 carbon atoms;

10 B is a hydrophilic monomer which has a vinyl group copolymerizable with said A monomer and is other than acrylic acid methacrylic acid, itaconic acid, acrylamide, methacrylamide, lower alkyl-substituted acrylamide, and N-vinyl-2-pyrrolidone, the amount of weight of B monomer being about 5 to 30% of the total weight of all monomers in the copolymer in the

15 copolymer; and

C is at least one polar monomer copolymerizable with said A and B monomers, selected from the group consisting of acrylic acid, methacrylic acid, itaconic acid, acrylamide,

20 methacrylamide, lower alkyl-substituted acrylamide and N-vinyl-2-pyrrolidone, the amount by weight of C monomer being about 0.5 to 30% of the total weight of all monomers in the copolymer;

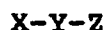
25 wherein said A, B and C monomers are copolymerized to form a polymeric backbone and the combination of A, B and C monomers being such as to be able to provide an adhesive-coated sheet material which has an initial dry

30 skin adhesion value of at least about 0.75 Newton per 100 millimeters of width, a dry skin adhesion value after 48 hours of not more than about 12 Newtons per 100 millimeters of width, and a moist skin adhesion value of at least about 2.2 Newtons per 100 millimeters of width.



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3. A sheet material according to Claim 1, wherein said B monomer is a hydrophilic macromolecular monomer having the general formula



5

wherein

X is a vinyl group copolymerizable with said A monomer;

Y is a divalent linking group; and

10

Z is a monovalent polymeric moiety comprising a polyether essentially unreactive under copolymerizing conditions; and wherein said polymeric backbone has pendant therefrom said polymeric moieties.

15

4. An adhesive-coated sheet material according to Claim 3, wherein said sheet material has a moist skin adhesion value of at least about 3 Newtons per 100 millimeters of width.

20

5. An adhesive-coated sheet material according to Claim 3, wherein said sheet material exhibits a moist skin adhesion value of at least about 4 Newtons per 100 millimeters of width.

25

6. An adhesive-coated sheet material according to Claim 5, wherein said sheet material exhibits a dry skin adhesion value of at least about 2 Newtons per 100 millimeters of width.

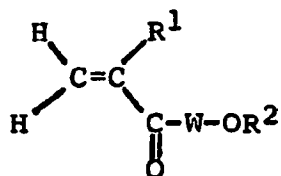
30

7. An adhesive-coated sheet material according to Claim 5, wherein said sheet material exhibits a dry skin adhesion value after 48 hours of not more than about 8 Newtons per 100 millimeters of width.



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8. An adhesive-coated sheet material according to Claim 3, wherein said B monomer is of the following formula



wherein R^1 is hydrogen or methyl; R^2 is hydrogen, lower alkyl, phenyl or substituted phenyl; and W is a divalent poly(alkylene oxide) group containing 2 to about 250 repeating alkoxide units and selected from the group consisting of a poly(ethylene oxide) radical, a poly(propylene oxide) radical, a radical of a copolymer of ethylene oxide and propylene oxide, and a polytetrahydrofuran radical, W being bonded covalently to the carbonyl group via a terminal oxygen atom contained in W.

9. An adhesive-coated sheet material according to Claim 3, wherein the weight of said hydrophobic monomer A is about 50 to 95% of the total weight of all monomers in said copolymer.

10. An adhesive-coated sheet material according to Claim 3, wherein the weight of said hydrophilic macromolecular monomer B is about 10 to 20% of the total weight of all monomers in said copolymer.

11. An adhesive-coated sheet material according to Claim 3, wherein the weight of said polar monomer C is about 5 to 20% of the total weight of all monomers in said copolymer.

12. An adhesive-coated sheet material according to Claim 3, wherein said backing is a nonwoven fabric, woven fabric, knit, paper, or synthetic film backing.



13. An adhesive according to Claim 2, wherein said B monomer is a hydrophilic macromolecular monomer having the general formula



5

wherein

X is a vinyl group copolymerizable with said A monomer;

Y is a divalent linking group; and

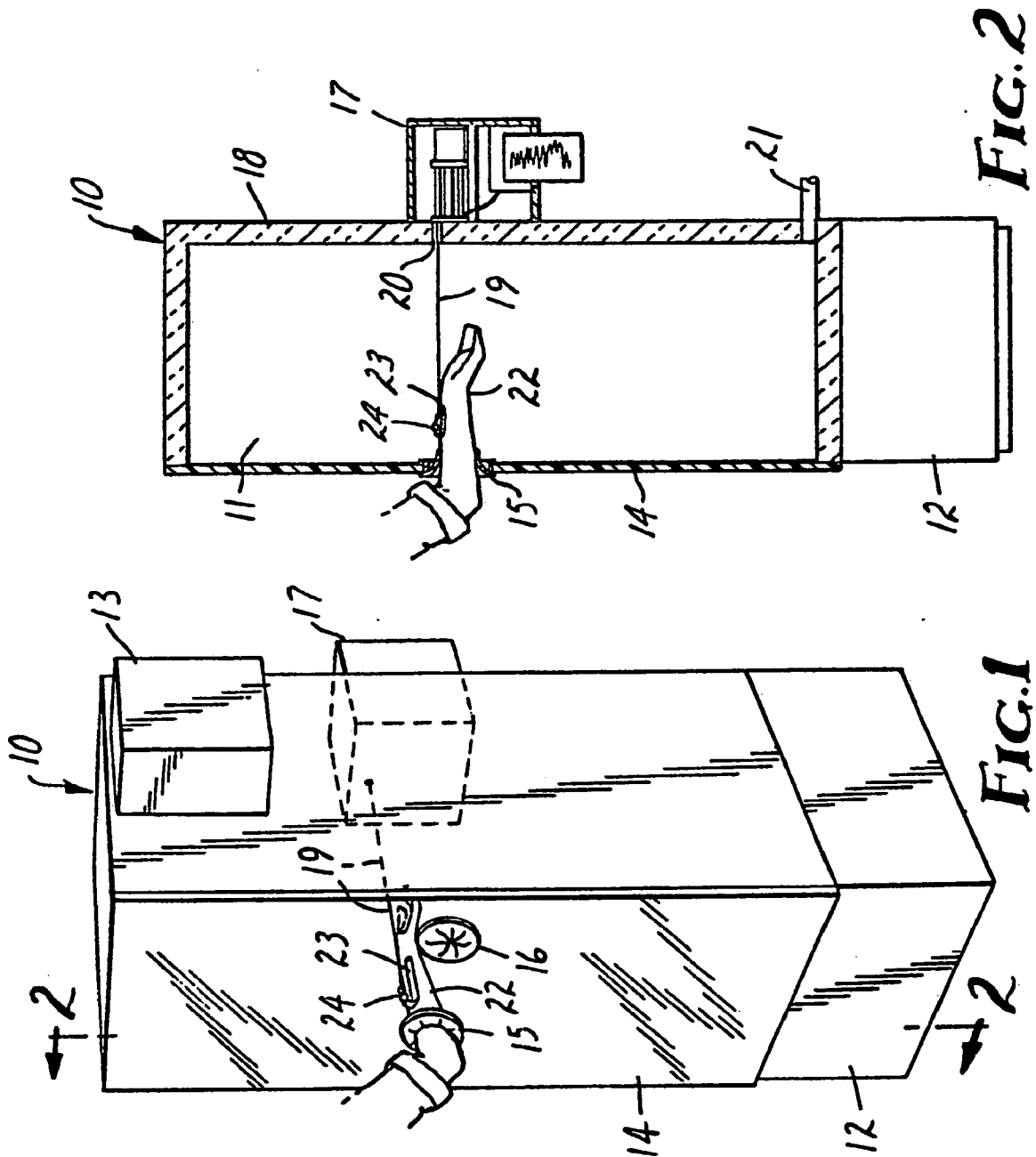
10

Z is a monovalent polymeric moiety comprising a polyether essentially unreactive under copolymerizing conditions; and

wherein said polymeric backbone has pendant therefrom said polymeric moieties.



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INTERNATIONAL SEARCH REPORT

International Application No **PCT/US 84/00506**

| I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) ³ According to International Patent Classification (IPC) or to both National Classification and IPC IPC³: A 61 L 15/06; C 09 J 3/14; C 08 L 33/08; C 08 F 299/02 | | | | | | | | | | | | | | | | | | | | |
|---|---|-------------------------------------|--|--|--|---|--|------------------|---|--|------|---|--|---|---|--|---|--|---|---|
| II. FIELDS SEARCHED <div style="text-align: center; margin-top: 10px;">Minimum Documentation Searched ⁴</div> <table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <th style="width: 20%;">Classification System</th> <th>Classification Symbols</th> </tr> <tr> <td style="text-align: center; vertical-align: top;">IPC³</td> <td>A 61 L; C 09 J; C 08 L; C 08 F</td> </tr> </table> <div style="text-align: center; margin-top: 10px;">Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁵</div> | | | Classification System | Classification Symbols | IPC ³ | A 61 L; C 09 J; C 08 L; C 08 F | | | | | | | | | | | | | | |
| Classification System | Classification Symbols | | | | | | | | | | | | | | | | | | | |
| IPC ³ | A 61 L; C 09 J; C 08 L; C 08 F | | | | | | | | | | | | | | | | | | | |
| III. DOCUMENTS CONSIDERED TO BE RELEVANT ¹⁴ <table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <th style="width: 10%;">Category ⁶</th> <th style="width: 60%;">Citation of Document, ⁸ with indication, where appropriate, of the relevant passages ¹⁷</th> <th style="width: 30%;">Relevant to Claim No. ¹⁸</th> </tr> <tr> <td></td> <td>US, A, 4077926 (SANDERSON F.T. et al.) 7 March 1978, see claims; examples; column 2, lines 40-61 --</td> <td style="text-align: center; vertical-align: top;">1-3, 8-11, 13</td> </tr> <tr> <td style="text-align: center;">Y</td> <td>FR, A, 2178760 (SALVE S.A.) 16 November 1973, see claims and examples --</td> <td style="text-align: center; vertical-align: top;">1, 2</td> </tr> <tr> <td style="text-align: center;">Y</td> <td>DE, A, 1934710 (T.J. SMITH & NEPHEW LTD.) 29 January 1970, see claims and examples --</td> <td style="text-align: center; vertical-align: top;">1</td> </tr> <tr> <td style="text-align: center;">Y</td> <td>US, A, 3121021 (COPELAND F.S.) 11 February 1964, see claims cited in the application --</td> <td style="text-align: center; vertical-align: top;">1</td> </tr> <tr> <td></td> <td>US, E, 24906 (ULRICH E.W.) 13 December 1960, see claims cited in the application -----</td> <td style="text-align: center; vertical-align: top;">1</td> </tr> </table> | | | Category ⁶ | Citation of Document, ⁸ with indication, where appropriate, of the relevant passages ¹⁷ | Relevant to Claim No. ¹⁸ | | US, A, 4077926 (SANDERSON F.T. et al.) 7 March 1978, see claims; examples; column 2, lines 40-61 -- | 1-3, 8-11, 13 | Y | FR, A, 2178760 (SALVE S.A.) 16 November 1973, see claims and examples -- | 1, 2 | Y | DE, A, 1934710 (T.J. SMITH & NEPHEW LTD.) 29 January 1970, see claims and examples -- | 1 | Y | US, A, 3121021 (COPELAND F.S.) 11 February 1964, see claims cited in the application -- | 1 | | US, E, 24906 (ULRICH E.W.) 13 December 1960, see claims cited in the application ----- | 1 |
| Category ⁶ | Citation of Document, ⁸ with indication, where appropriate, of the relevant passages ¹⁷ | Relevant to Claim No. ¹⁸ | | | | | | | | | | | | | | | | | | |
| | US, A, 4077926 (SANDERSON F.T. et al.) 7 March 1978, see claims; examples; column 2, lines 40-61 -- | 1-3, 8-11, 13 | | | | | | | | | | | | | | | | | | |
| Y | FR, A, 2178760 (SALVE S.A.) 16 November 1973, see claims and examples -- | 1, 2 | | | | | | | | | | | | | | | | | | |
| Y | DE, A, 1934710 (T.J. SMITH & NEPHEW LTD.) 29 January 1970, see claims and examples -- | 1 | | | | | | | | | | | | | | | | | | |
| Y | US, A, 3121021 (COPELAND F.S.) 11 February 1964, see claims cited in the application -- | 1 | | | | | | | | | | | | | | | | | | |
| | US, E, 24906 (ULRICH E.W.) 13 December 1960, see claims cited in the application ----- | 1 | | | | | | | | | | | | | | | | | | |
| <div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>⁹ Special categories of cited documents: ¹⁵</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 50%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"A" document member of the same patent family</p> </div> </div> | | | | | | | | | | | | | | | | | | | | |
| IV. CERTIFICATION <table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 50%; padding: 5px;"> Date of the Actual Completion of the International Search ³ <div style="text-align: center; font-weight: bold;">25th June 1984</div> </td> <td style="width: 50%; padding: 5px;"> Date of Mailing of this International Search Report ³ <div style="text-align: center; font-weight: bold;">07. 08. 84</div> </td> </tr> <tr> <td style="width: 50%; padding: 5px;"> International Searching Authority ¹ <div style="text-align: center; font-weight: bold;">EUROPEAN PATENT OFFICE</div> </td> <td style="width: 50%; padding: 5px;"> Signature of Authorized Officer ¹⁹ <div style="text-align: center;"> <div style="text-align: right; font-weight: bold;">G.L.M. Kruidenberg</div> </div> </td> </tr> </table> | | | Date of the Actual Completion of the International Search ³ <div style="text-align: center; font-weight: bold;">25th June 1984</div> | Date of Mailing of this International Search Report ³ <div style="text-align: center; font-weight: bold;">07. 08. 84</div> | International Searching Authority ¹ <div style="text-align: center; font-weight: bold;">EUROPEAN PATENT OFFICE</div> | Signature of Authorized Officer ¹⁹ <div style="text-align: center;"> <div style="text-align: right; font-weight: bold;">G.L.M. Kruidenberg</div> </div> | | | | | | | | | | | | | | |
| Date of the Actual Completion of the International Search ³ <div style="text-align: center; font-weight: bold;">25th June 1984</div> | Date of Mailing of this International Search Report ³ <div style="text-align: center; font-weight: bold;">07. 08. 84</div> | | | | | | | | | | | | | | | | | | | |
| International Searching Authority ¹ <div style="text-align: center; font-weight: bold;">EUROPEAN PATENT OFFICE</div> | Signature of Authorized Officer ¹⁹ <div style="text-align: center;"> <div style="text-align: right; font-weight: bold;">G.L.M. Kruidenberg</div> </div> | | | | | | | | | | | | | | | | | | | |

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON

INTERNATIONAL APPLICATION NO. PCT/US 84/00506 (SA 6997)

This Annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 01/08/84

The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

| Patent document cited in search report | Publication date | Patent family member(s) | Publication date |
|--|---------------------|----------------------------|---------------------|
| US-A- 4077926 | 07/03/78 | None | |
| FR-A- 2178760 | 16/11/73 | NL-A- 7204517 | 09/10/72 |
| | | DE-A- 2216260 | 02/11/72 |
| | | GB-A- 1381185 | 22/01/75 |
| | | CH-A- 581673 | 15/11/76 |
| DE-A- 1934710 | 29/01/70 | NL-A- 6910564 | 13/01/70 |
| | | FR-A- 2012584 | 20/03/70 |
| | | GB-A- 1280631 | 05/07/72 |
| | | US-A- 3645835 | 29/02/72 |
| | | CH-A- 526306 | 29/09/72 |
| | | BE-A- 735782 | 08/01/70 |
| | | SE-B- 127578 | 03/12/73 |
| | | SE-B- 377887 | 04/08/75 |
| US-A- 3121021 | | None | |
| US-E- 24906 | | None | |

For more details about this annex :
see Official Journal of the European Patent Office, No. 12/82